# Transition from heterogeneous catalytic reaction to homogeneous one by variation of palladium particle size

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Abstract

Reduction of methylene blue with hydrazine was catalyzed by nearly mono-dispersed palladium particles of which diameters ($2r_0$) ranged from 30 to 230 nm. The spectroscopically evaluated pseudo-first order reaction rate constants were proportional to $r_0^{3\alpha}$, where $3\alpha$ varied from 2 to 3 with a decrease in the radius. The catalysis at large $r_0$ proceeded heterogeneously, whereas that at small $r_0$ occurred homogeneously. The relation between $\alpha$ and $r_0$ allowed us to evaluate the thickness of the reaction layer to be 20 nm. The analysis of the diffusion-reaction model demonstrated the thickness did not vary largely with $r_0$.

*Keywords*: catalysis by palladium particles, methylene blue, reaction order, thickness of reaction layer

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## Introduction

Catalysis is classified into the heterogeneous catalysis and the homogeneous one [1,2]. Since a reaction rate of the former reaction is controlled by the surface area of the catalyst, a decrease in the size of the catalyst increases the surface area, leading to the enhancement of the reaction rate. The enhancement has been realized in nano-sized catalysts [3- 11]. If the size is decreased up to a molecular level, the reaction may behave as a homogeneous reaction, of which reaction rate is not controlled by the area of the catalyst but is governed by the volume concentration. From the practical viewpoint, the decrease in size is limited by keeping recovery and recyclability of catalytic materials [12].

When a homogeneous catalytic reaction occurs in a volume, $V$, which contains $n$ spherical catalysts in radius $r_0$, the reaction rate is proportional to the volume ratio of the catalyst, $n(4\pi r_0^3/3)/V$. If a heterogeneous reaction occurs in the same conditions as above, its rate is proportional to the surface area, $n(4\pi r_0^2)/V$. We want to connect the heterogeneous rate with the homogeneous one smoothly by compensating the difference in the dimensions. When the reaction layer thickness, $\delta$, is introduced, the heterogeneous rate is proportional to $n(4\pi r_0^2)\delta/V$. Then the dimension in the two rates becomes common, and hence the ratio of the heterogeneous one to the homogeneous one, $3\delta/r_0$, is an measure of a feature of the mode of the catalysis. The concept of the reaction layer has been applied to analyzing reaction mechanisms in electrochemical fields [13,14]. It is worth while noting that the layer is different from thickness of catalytic layers [15,16,17].

We may realize the variation from the heterogeneous reaction to the homogeneous one by changing diameters of palladium particle as a catalyst because size of Pd nanoparticles can be altered synthetically [18]. This communication deals with measurements of the rates of the catalytic reduction of methylene blue by hydrazine with the aid of solution-dispersed palladium particles [19,20,21]. We discuss the dependence of the rate constant on the size in the context of connecting the heterogeneous reaction to the homogeneous one.

## Experiments

All the chemicals and synthetic process of palladium particles were basically the same as those described previously [19]. Size of palladium nanoparticles has been decreased with an increase in concentration of a surfactant, poly(*N*-vinyl pyrrolidone) (PVP) [18]. 100 $cm^3$ Ethanol solution including 20 mg palladium acetate was mixed with 100 $cm^3$ water containing 80, 120, 160 or 180 mg PVP, exhibiting yellow color. The mixture, to which 5 mg hydrazine was added, was refluxed for 5 h, cooled, centrifuged, rinsed, and re-dispersed in water. The formed suspension in ethanol was filtrated by means of microfilter with 0.2 μm pores to exhibit black transparent. The particle size distribution was obtained with Zetasizer Nano S90 (Malvern Instruments Ltd. UK).

The kinetics of the catalytic reaction was examined by mixing methylene blue with a given amount of hydrazine and a given amount of several kinds of Pd particles. The maximum absorption of methylene blue at 664 nm was obtained at various reaction periods with a UV-vis spectrometer, UV-570 (JASCO) at 20 $^oC$. The background to be subtracted was the absorption without methylene blue.

## Results and discussion

The suspensions synthesized in the ethanol including 80, 120, 160 and 180 mg PVP contained particles 230, 105, 56 and 34 nm in average diameter, respectively. The relations between the particle size and concentration of PVP were qualitatively in accord with the prediction [18]. Quantitatively, the square of the radius was inversely proportional to the concentration of PVP. That is, the particle size was controlled so that the amount of PVP adsorbed on one particle was common.

We applied the Pd particles to catalytic reduction of methylene blue by hydrazine in aqueous solution, as Pal et al. sis [20,21]. The vis-spectral band at 664 nm for methylene blue did not shift by addition of hydrazine and Pd particles, and hence neither influence of

side reaction nor light scattering of the Pd particles need to be taken into account [19,21]. The absorbance, $A$, of this band decreased logarithmically with the reaction time, $t$, as is shown in Fig.1, where the ordinate was normalized with the absorbance at $t$ = 0. The proportional variation of ln $A$ with the time suggests the first-order kinetics with respect to methylene blue. The coefficient of the proportionality, corresponding to the quasi-first-order reaction rate constant, $k$, increased with the concentration of Pd particles, $c$.

In order to examine the dependence of $k$ on $c$ accurately, we subtracted the rate constant without Pd particle, $k_0$, from the rate constants with Pd particles. The values of $k$-$k_0$ were plotted against $c$ on the logarithmic scale in Fig.2. They show linear variations, indicating that $k$-$k_0$ should be proportional to the power of the concentration, or

$$k - k_0 = K_1 c^{\alpha} \qquad (1)$$

where $K_1$ is a constant. Values of $\alpha$ increased from 0.71 to 0.99 as the radii of particles decreased, as is shown in Fig.3. Letting the weight of the one particle be $w$, the density be $d$, the number of particles be $n$ in the volume $V$ of the suspension, and the radius of the particle be $r_0$, then we have the following equality:

$$c^{\alpha} = (nw/V)^{\alpha} = \left(n(4\pi/3)r_0^3 d/V\right)^{\alpha} = (\text{const})r_0^{3\alpha} \qquad (2)$$

The rate constant for $\alpha = 1$ is proportional to $r_0^3$ or the volume of the particle, whereas that for $\alpha = 2/3$ is proportional to $r_0^2$ or the surface area of the particle. The variation of $3\alpha$ from 3 to 2 in Fig.3 indicates the reaction ought to vary from a volume reaction to a surface reaction with an increase in the radii.

The intermediate reaction ($2 < 3\alpha < 3$) observed belongs neither to a homogeneous reaction nor to a heterogeneous reaction [1]. If heterogeneous reaction layers are accumulated to a volumetric porous layer, they may reveal apparently the property of a homogeneous reaction. In contrast, when a homogeneous layer is blocked so that only a thin layer works as a catalyst, it may reveal apparently a heterogeneous reaction. Therefore an intermediate reaction occurs when a layer works as the actual catalysis.

We apply this concept to our particles by assuming that the thickness, $\delta$, from the surface of the sphere functions as the reaction layer. This situation occurs when methylene

blue can penetrate into this layer together with hydrazine to be catalyzed with Pd. The volume relevant to the reaction is given by

$$V_r = (4\pi/3)\{r_0^3 - (r_0 - \delta)^3\} \approx 4\pi r_0 \delta (r_0 - \delta) \quad (3)$$

where the term of $\delta^3$ was neglected for $\delta < r_0$. Since this volume is proportional to the reaction rate constant, we have from Eq.(1)-(3) the following a series relation

$$k - k_0 = K_1 c^{\alpha} = K_2 r_0^{3\alpha} = K_3 r_0 \delta (r_0 - \delta) \quad (4)$$

where $K_2$ and $K_3$ are constants. Dividing the third and the forth term in Eq.(4) by $r_0$ yields

$$r_0^{3\alpha-1} = (K_3 / K_2)\delta (r_0 - \delta) \quad (5)$$

We plotted the variation of $r_0^{3\alpha-1}$ with $r_0$ on the right-upper axes in Fig.3. In accord with Eq.(5), the plot fell in a straight line. The linearity supports invariance of the thickness of the reaction layer to the radii. Since the slope and the intercept of the linearity are $(K_3/K_2)\delta$ and $-(K_3/K_2)\delta^2$, respectively, the ratio -[intercept]/[slope] gives $\delta$. From the values of the intercept and the slope in Fig.3, we obtained $\delta = 20 \pm 5$ nm.

We explain the invariance of $\delta$ to $r_0$ in terms of the diffusion-reaction model, in which methylene blue diffuses into the Pd particle to react with hydrazine on the Pd catalytic site. The concentration of methylene blue, $z$, within the particle ($r < r_0$) obeys the diffusion-reaction equation in the polar coordinate:

$$\frac{\partial z}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left( r^2 \frac{\partial z}{\partial r} \right) - kz \quad (6)$$

where $D$ is the diffusion coefficient of methylene blue in the particle and $r$ is the radial distance from the center of the particle. It is assumed that the time-variation of $z$, is much faster than that of the bulk concentration, $c$. Then Eq.(6) is regarded as the steady state, $\partial z/\partial t = 0$. A solution of Eq.(6) under the steady state is

$$rz = A_1 \exp\left(\sqrt{k/D}\, r\right) + A_2 \exp\left(-\sqrt{k/D}\, r\right) \quad (7)$$

where $A_1$ and $A_2$ are constants. Application of the boundary condition of a finite value of $(z)_{r=0}$ yields $A_1 + A_2 = 0$. Applying the condition that the concentration at the surface of the particle is equal to that of the bulk, i.e., $(z)_{r=r0} = c$, we obtain an explicit expression of $A_1$. Then we have

$$z/c = (r_0/r)\left[\sinh\left(\sqrt{k/D}r\right)/\sinh\left(\sqrt{k/D}r_0\right)\right] \quad (8)$$

The variation of the normalized concentration with $r/r_0$ is shown in Fig.4 for $(k/D)^{1/2}r_0 = 8$. The concentration decreases sharply from $z = c$ at $r = r_0$ with a decrease in $r$, and tends to

$$c_{\text{in}}/c \to \left(\sqrt{k/D}r_0\right)/\sinh\left(\sqrt{k/D}r_0\right) \text{ for } r \to 0$$

We define the thickness of the reaction layer to be the domain between the surface and the intercept of the tangent line at $r = r_0$ on the abscissa, as is shown in Fig.4 (dashed line). Since the slope of the tangent line is $(c/r_0)((k/D)^{1/2}r_0 \coth[(k/D)^{1/2}r_0]-1)$, the dimensionless thickness of the reaction layer is expressed by

$$\sqrt{k/D}\delta = \frac{\sqrt{k/D}r_0}{\sqrt{k/D}r_0 \coth\left(\sqrt{k/D}r_0\right)-1} \quad (9)$$

This is a function of $(k/D)^{1/2}r_0$, of which variation is shown in Fig.5. Values of $(k/D)^{1/2}\delta$ tend to unity with an increase in $(k/D)^{1/2}r_0$. The invariance of the experimental value of $\delta$ (= 20 nm) with $r_0$ indicates that $(k/D)^{1/2}\delta$ is closed to unity. Then we have approximately $k/D$ = $(1/20\text{ nm})^2$. Since $k$ is of the order of $10^{-2}$ $s^{-1}$ from Fig.2, a value of $D$ is close to $10^{-12}$ $cm^2$ $s^{-1}$. This value is conventional for the diffusion coefficient in solids.

## Conclusion

The catalytic reaction rate constants of methylene blue with hydrazine increased with a decrease in the diameter of Pd particles. This variation can be explained in terms of the increase in the surface area of the Pd particles. The reaction order with respect to the Pd particles varied from 0.7 to 1 with a decrease in the size of the particle. This variation is equivalent to that from a surface (heterogeneous) reaction to a volume (homogeneous) one. The analysis of the dependence of the reaction order on the radii allowed us to estimate the thickness of the reaction layer. Since thickness did not vary with the radii, it can be regarded as a feature proper to the kinetics. The analysis of the diffusion-reaction model supported the invariance of the thickness to the radii.

Palladium particles with several diameters were synthesized by reducing palladium acetate with hydrazine in the presence of different amount of PVP. The average diameters were 230, 105, 56 and 34nm. The radii were controlled with the concentration of PVP so that $r_0^2 c$ was constant. This relation suggests a significant contribution of surface process to the size control.

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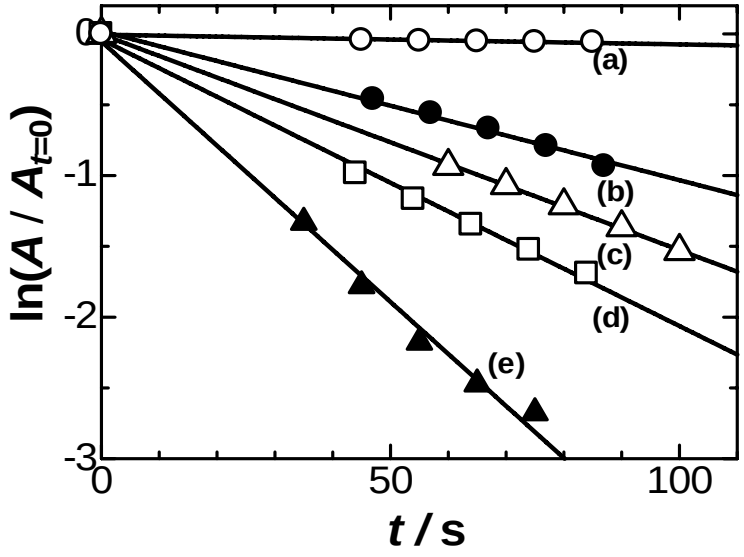


Figure 1

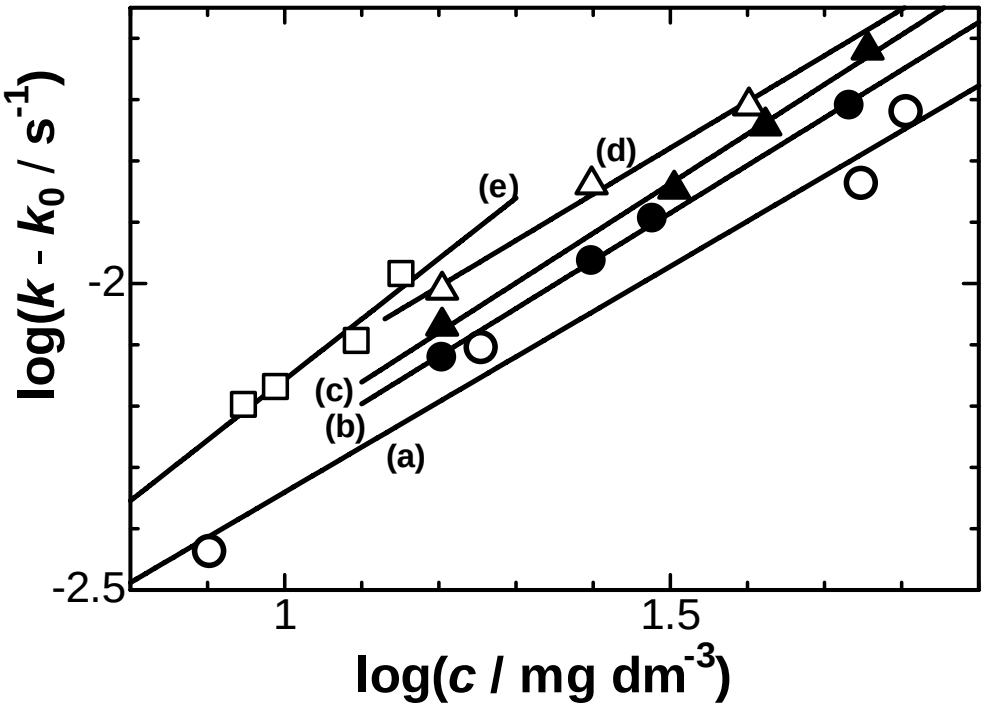


Figure 2

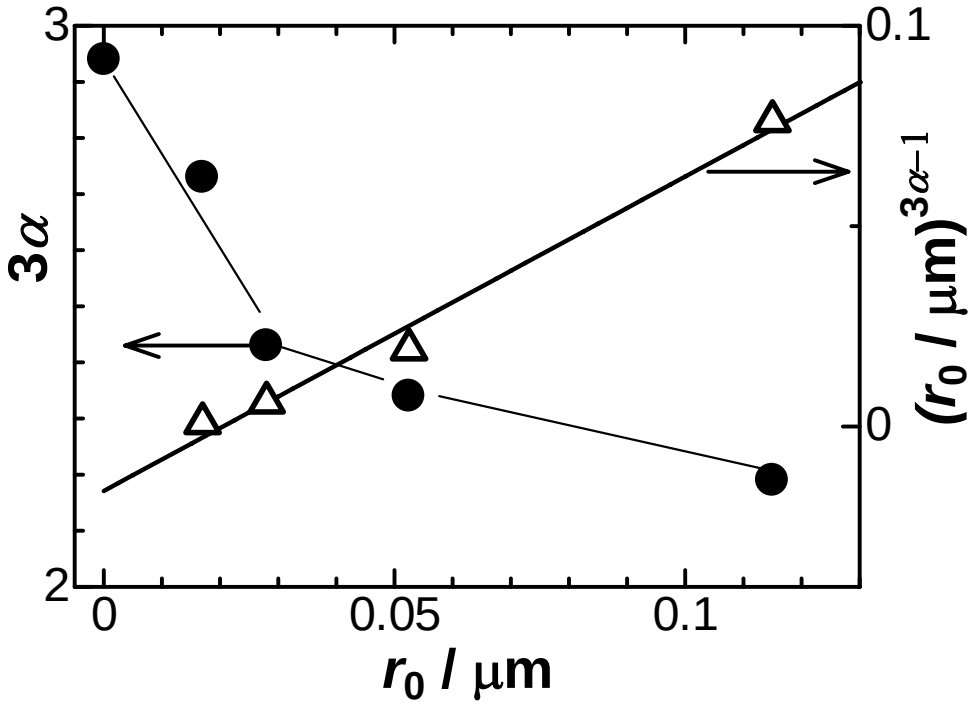


Figure 3

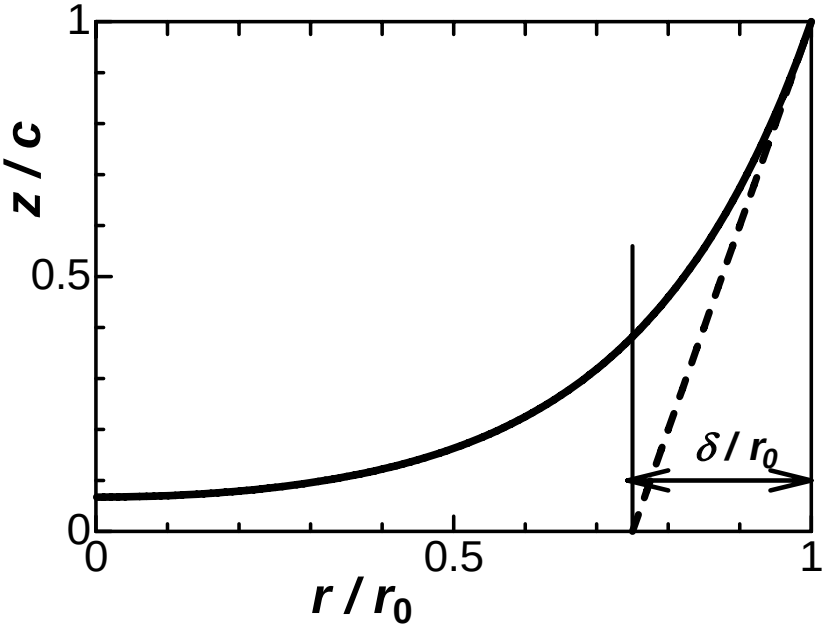


Figure 4

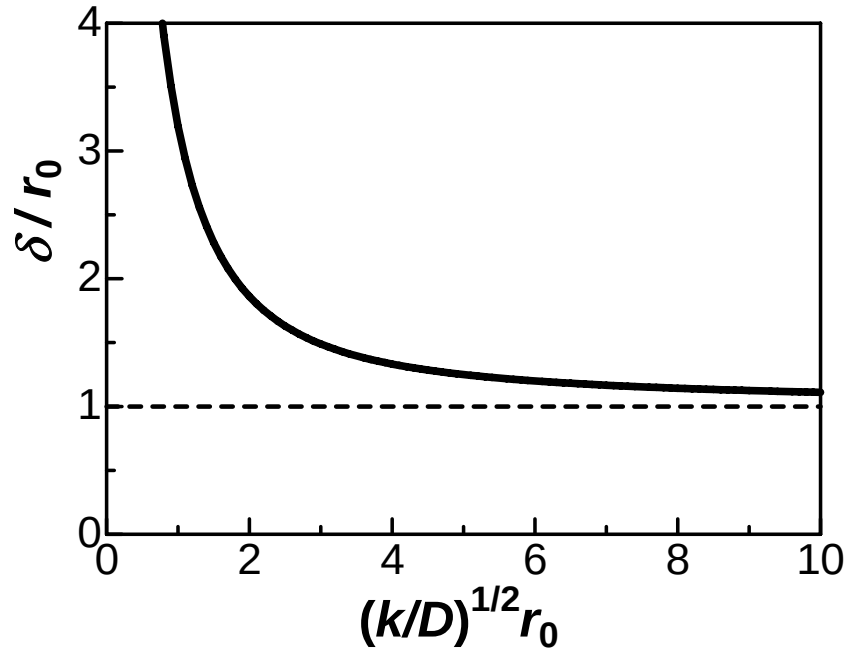


Figure 5

## Figure Captions

Figure 1. Logarithmic dependence of the absorbance at 664 nm of the mixture of 9 μM methylene blue and 4 mM hydrazine on the reaction time. The solution contained (a) 0, (b) 16, (c) 25, (d) 40, (e) 64 mg $dm^{-3}$ Pd particles with $2r_0$ = 34 nm.

Figure 2. Logarithmic dependence of the first-order reaction rate constants on concentration of Pd particles for with $2r_0$ = (a) 230, (b) 105, (c) 56 and (d) 34 nm, and (e) of $PdCl_2$. The rate constants of reaction were obtained from the slopes of Figure 1.

Figure 3. Dependence of the reaction order, $\alpha$, of the rate constant (circles) on the radii on the Pd particles, and the plot of $r_0^{3\alpha-1}$ (triangles) against $r_0$ in Eq.(5).

Figure 4. Concentration profile of methylene blue in the particle, and the tangent (dashed) line defining the thickness of the reaction layer.

Figure 5. Dependence of the thickness of the reaction layer on the radii.